



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> LUBRICIOUS HYDROPHILIC COATING, RESISTANT TO WET ABRASION  <b>(57) Abstract</b>  The lubricious hydrophilic coatings of the invention are significantly more lubricious when wet than when dry, are adherent to a variety of substrates, and are resistant to removal by wet abrasion. In one embodiment, the coatings include a hydrophilic polyolefin such as polyvinyl-pyrrolidone and a water-insoluble stabilizing polymer such as a cellulose ester. The coatings may also include an adherent polymer and a plasticizing agent. The coating may be applied by preparing a solution of the stabilizing polymer and a solution of the hydrophilic polyolefin, and coating the substrate first in one then the other. Alternatively, both the stabilizing and hydrophilic polymers may be dissolved in a single solvent system and applied to the substrate in a single step. In another embodiment, only a solution of a hydrophilic polyolefin is applied directly to the substrate. In this embodiment, the solution of the hydrophilic polyolefin includes a cosolvent which acts as a solvent for both the hydrophilic polyolefin and the substrate. The coatings of the invention may be applied to biomedical devices and implants such as catheters, condoms, and nasogastric and endotracheal tubes.		

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LUBRICIOUS HYDROPHILIC COATING,  
RESISTANT TO WET ABRASION

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BACKGROUND OF THE INVENTION

This invention relates to hydrophilic, lubricant coatings that make biomedical devices slippery when wet. The method and coating of the invention may be employed to reduce the coefficient of friction of catheters, condoms, contact lenses, peristaltic pump chambers, arteriovenous shunts, gastroenteric feed tubes and endotracheal tubes, or other implants of metal or polymer substrate.

Known lubricious coatings that may be applied to biomedical devices include coatings of polyvinylpyrrolidone (PVP), polyurethane, acrylic polyester, vinyl resin, fluorocarbons, silicone, rubber, or combinations of these substances. For example, Micklus et al., U.S. 4,100,309 and U.S. 4,119,094 relate to a hydrophilic coating of PVP polyurethane interpolymer formed with polyisocyanate. Ratner et al., U.S. 3,939,049, relates to a method of grafting hydrogels to polymeric substrates using radiation. Hudgin et al., U.S. 3,975,350, relates to hydrophilic polyurethane polymers. Stoy et al., U.S. 3,987,497,

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relates to a tendon prosthesis with hydrogel coating.

These known hydrogel coatings have disadvantages: They may have an insufficiently low coefficient of friction, they may lack permanence (such as silicone or fluorocarbons), they may be slippery when dry as well as wet, making handling difficult, or (such as the Micklus et al. coatings) they may require the use of hazardous solvents to prepare them and contain unstable, reactive materials, so that separate and new solutions must be prepared daily or more frequently.

Furthermore, in the PVP-polyurethane coatings, little control can be exerted over the degree of lubricity and resistance to wet abrasion of the coatings, and such coatings are often unstable.

In order to solve these problems a hydrophilic lubricant coating was needed which, when wetted, has sufficient lubricity to be useful for biomedical devices such as implants, which adheres to a wide variety of substrates and resists wet abrasion, and which can be prepared from chemically stable and biocompatible solvents.

#### SUMMARY OF THE INVENTION

One embodiment of the present invention relates to a hydrophilic coating which comprises a hydrophilic polymer and a stabilizing polymer in a layer bonded to the surface of the device. The hydrophilic polymer is a polyolefin such as a vinyl polymer having polar pendant groups, a polyacrylate or methacrylate having hydrophilic esterifying groups, a polyether, a polyethylene glycol, or other polyolefin with hydrophilic characteristics. The hydrophilic polymer is

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preferably PVP or PVP vinyl acetate. The stabilizing polymer is a water-insoluble polymer that does not significantly react with the hydrophilic polymer in solution, and is preferably cellulose ester, a copolymer of polymethyl vinyl ether and maleic anhydride, or nylon. The cellulose esters are most preferred. They include ethyl cellulose, hydroxyethyl cellulose, cellulose nitrate, cellulose acetate, cellulose acetate butyrate, and cellulose acetate proprionate.

10 In one embodiment, the coating has an inner layer where the stabilizing polymer is concentrated and an outer layer where the hydrophilic polymer is concentrated. In another embodiment, the hydrophilic polymer and stabilizing polymer are contained in a single application and comprise a single layer of coating.

The coating may also contain an adherent polymer such as polyurethane, polyester, styrene polybutadiene, acrylic resin, polyvinylidene chloride, polycarbonate, and polyvinyl chloride, preferably in the inner layer to promote adhesion to the surface of the device.

A most preferred outer layer composition uses PVP of high molecular weight (e.g. 120,000-360,000).

The inventive coating may be applied to a polymer surface such as polyurethane, polyvinyl chloride, polyacrylate, polycarbonate, polystyrene, polyester resin, polybutadiene-styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon, and polyvinyl acetal. The coating of the invention can also be applied to glass or metals such as stainless steel. The coating components can be selected to produce a coating with desired properties on these surfaces.

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The method of preparing the coatings of the invention employs stable, non-toxic solutions which may be stored and handled with minimal precautions. The method of applying the coating of the invention  
5 comprises preparing a first organic solution of from about 0.01% to about 30% weight to volume of stabilizing polymer, preferably from about 0.2% to about 10%, applying the solution to a substrate surface, and evaporating the solvent, preferably at elevated  
10 temperature, then preparing a second solution of from about 0.01% to about 30% weight to volume hydrophilic polymer, preferably from about 0.5% to about 20%, applying it to the treated surface substrate and evaporating the solvents at room or elevated  
15 temperature.

The stabilizing polymer solution may also contain from about 0.01% to about 10% of hydrophilic polymer, preferably from about 0.1% to about 5%. The hydrophilic polymer solution may also contain from about 0.01% to  
20 about 20% of stabilizing polymer, preferably from about 0.1% to about 10%. Alternatively, the stabilizing polymer and hydrophilic polymer can be prepared in a single solution and applied in a single step.

The surface of the device may be pre-treated to  
25 promote adhesion of the coating. The solutions may also contain from about 0.1% to about 15% of an adherent polymer, preferably from about 1.0% to about 8.0% weight to volume to promote the bond between substrate and coating.

30 A plasticizing agent may be included with the stabilizing polymers, in a concentration of from about 0.01% to about 10%, preferably from about 0.1% to about

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5.0%, weight to volume. The plasticizing agent may be camphor, castor oil, dioctyl phthalate, acetyl tributyl citrate, dibutyl sebacate, sebacic acid, alkyl resin, dibutylphthalate, polyvinylbutyral or other commonly known plasticizers, singly or in combination. The plasticizing agent is preferably included in the solution of stabilizing polymer. The inventive coating may include a plasticizer to enhance the flexibility of the coating, which may be preferable when the object to be coated is likely to bend during use. Also, the inclusion of a plasticizer is preferred when the stabilizing polymer is nitrocellulose, because the plasticizer reduces the tendency of nitrocellulose to oxidize rapidly or even combust when it is dried in a pure form.

Solvents for the stabilizing and adherent polymer include organic solvents such as ketones, esters, toluene, lactones, dimethylformamide, halogenated solvents, tetrahydrofuran, dioxane, amines, glycol butyl ether, alkyl acetates, acetonitrile, and other commonly known organic solvents. The less toxic solvents are preferred. The inclusion of small amounts of hydroxyl groups such as alcohols and moisture in the solvent does not have a significant detrimental effect on the coating and method of the invention.

Solvents for the hydrophilic polymer include most of the above as well as alcohols, acetic acid, and like solvents. A solvent system may be selected that is capable of dissolving all the constituents of the coating in a uniform solution, can act as a co-solvent in the layer, and is non-toxic.

If desirable, a solvent may be selected that

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interacts with the particular substrate surface to promote adhesion.

In another embodiment of the present invention, the article to which the coating is to be applied has a polymer surface and an "active" solvent is used which obviates the need for the inner layer or base coat by permitting a lubricious hydrophilic layer (or top coat) to be applied directly onto the polymer surface of the article. In this embodiment, the term "active solvent" is defined as a cosolvent for both the polymer or polymer mixture comprising the polymer surface or at least one or more of the polymers in cases of mixed polymer substrates and for the coating polymer(s).

The solutions may be applied by dipping the object to be coated into a vessel containing the solution, or the solutions may be poured, pumped, brushed or sprayed onto the object.

#### DETAILED DESCRIPTION OF THE INVENTION

The hydrophilic coatings of this invention are highly lubricious when wetted with an aqueous solution such as body fluid, or a lower alcohol such as ethanol or methanol, yet they are substantially less slippery when dry. Thus, an implant coated according to the invention remains non-slippery for ease of handling and preparation, but becomes lubricious when implanted, so as to protect the patient. The lubricity of the coating can be adjusted within a desirable range.

A coating according to the invention may be applied to the surface of a biomedical or other device with sufficient thickness and permanence to retain the coating's desirable qualities throughout the useful life



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of the coated device. The coatings of the invention are non-reactive with living tissue and are non-thrombogenic in blood.

The coating of the invention has beneficial characteristics for use on the surfaces of devices such as biomedical implants. The coating is hydrophilic, absorbing water and swelling in an aqueous environment to become a hydrogel. The coating has lubricant properties, and is significantly more slippery when wet than when dry. The coating is thin, on the order of magnitude of one thousandth of an inch. The coating is coherent and resistant to removal by wet abrasion, and it is adherent to a wide variety of substrates. The coating employs biocompatible substances that are neither toxic nor irritant. The functional characteristics of the coating may be varied as appropriate for many different applications.

The method of the invention is beneficial because the components can be varied to control lubricity, swelling, flexibility, and resistance to removal by wet abrasion. These characteristics of the coating can thus be adjusted for various substrates and applications. The method is also beneficial because the solutions of the invention have good shelf stability and remain substantially free of precipitate for periods in the range of months or years, so that various mixtures of the solutions for coatings may be prepared at one time and used to coat substrates later. Alternatively, the hydrophilic and stabilizing polymers, and if desired, a plasticizing agent and an adherent polymer, may even be prepared in a single solution. Furthermore, since the invention does not require the use of chlorinated

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solvents or other acute toxics, fewer precautions are necessary to protect workers from health hazards.

Without intending to limit the invention to its mode of operation, apparently the stabilizing polymers of the invention, particularly modified cellulose polymers, are able to make hydrophilic polymers, such as PVP and PVP-vinyl acetate copolymers, stable and insoluble in water and lower alcohols. The resulting combination, when applied to a substrate, produces a coating that is a stable layer or layers that are bonded to a substrate surface, is not slippery when dry but is desirably lubricious when wet, and is resistant to removal by conditions of wet abrasion. The coating layer bonds to an impervious surface such as stainless steel or glass. It also bonds to polymer surfaces where the surface interacts with the components of the coating.

It is possible to control the degree of stability, wet lubricity, insolubility, flexibility, and adhesion of the coating by varying the weight to volume percentages of the components in the coating solutions. Substantially all of the polymers and plasticizers deposited from solutions onto the surface of the object being coated remain in the layer of the coating after the solvents are evaporated. Also, the duration and temperature of the evaporating step may be selected to achieve stability of the coating layer and to achieve a bond between the surface being coated and the coating layer.

Preferably, the outer layer solution contains some amount of an "active" solvent, i.e., a cosolvent, for the outer layer ingredients as well as the inner layer

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ingredients. As such, the active solvent causes the outer layer solution to penetrate into the inner layer, and is believed to bring about a mixing at the molecular level of the components of both layers.

5 It is believed that such molecular mixing may lead to chemical reactions such as cross-linking between the components, or may only comprise physical mixing without chemical reaction(s). In any event, in one preferred embodiment, there is a high degree of cross-linking or  
10 intermolecular mingling between the hydrophilic polymer and the stabilizing polymer at the interface between the inner and outer layers of the coating relative to the outer surface of the outer layer. Thus, an interpolymer between the two layers may be created as a result of  
15 cross-linking or intermolecular mingling between the polymers contained in the separate layers. The slight degree or lack of cross-linking at the outer surface of the coating aids in providing the lubricity of the coating of the present invention.

20 In practice, the activity of the solvent mixture is adjusted so that the degree of penetration of the outer layer into the inner layer is in a useful range. For example, if the outer layer solvent mixture is too active toward the inner layer, then too much penetration  
25 into the inner layer occurs, and the outer layer will not be sufficiently lubricious when wet. Conversely, if the outer layer solvent is too inactive toward the inner layer, then too little penetration of outer layer into the inner layer occurs, and the coating is too easily  
30 removed from the inner layer by wet abrasion.

In another embodiment of the present invention, where the lubricious hydrophilic layer is applied

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directly onto a polymer surface as a top coat, and an active solvent is used which is a cosolvent for both the plastic substrate polymer or polymer mixture or at least one or more of the polymers in cases of mixed polymer substrates, and for the coating polymer(s) in the hydrophilic layer.

After drying, which is typically done at temperatures between 50°C and 100°C, but may be done at higher or lower temperatures, the top coat polymer(s) layer is left partially embedded in the polymer surface. As in the case of the two-layer system, the solvent used during the coating application can be too active such that the top coat penetrates into the polymer surface to such a degree that the coated layer behaves as though it has been highly cross-linked. This causes the top coat to not become sufficiently swollen and lubricious when wet by aqueous fluids. Solvent mixtures can also be too inactive, so that the coating is not resistant enough to abrasion when wet and is too easily removed.

As in the two-layer systems, other polymers or cross-linking agents may be incorporated with the hydrophilic polymer(s) in the lubricious layer to enhance the adhesion of the layer to the polymer surface, making the lubricious layer more resistant to wet abrasion.

The active solvents which are useful in the present invention may be individual solvents or solvent mixtures containing two or more solvents. In the case of solvent mixtures, one or more of the solvents in the mixture may be active while other solvent(s) in the mixture may be inactive. In any event, the solvent or solvent mixture dissolves or at least disperses the top coat polymer(s).

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In cases where the top coat polymer is dispersed but not dissolved, a point is reached where the top coat polymer(s) go into solution before all of the solvent has left the coating. During the phase of drying where the top coat polymer(s) is in solution, the solvent has also penetrated the substrate polymer(s) of the polymer surface. Thus, intermolecular mingling may take place between the substrate polymer(s) and the top coat polymer(s).

Examples of active solvents useful in the present invention include butyrolactone, alcohols, dimethyl acetamide, and n-methyl-2-pyrrolidone. These solvents and others cause different degrees of swelling of the plastic substrate or inner layer, as the case may be.

The hydrophilic polymers of the coatings are generally PVP of higher molecular weight, 120,000-360,000. PVP of lower molecular weight, as low as 15,000, can be used in the underlayer or base coating next to the substrate without deterioration of performance. Some or all of the PVP can be replaced with PVP-vinylacetate copolymer in the one-coat embodiment, or in either layer of the two-coat embodiment.

It has been found that the most preferred stabilizing polymer is a water insoluble cellulose polymer. Alternatives to modified cellulose polymers, such as polymethylvinylether maleic anhydride and nylon may be used instead of or in addition to the modified cellulose polymers, but these are more difficult to work with, and tend to produce coatings with less long-term wet abrasion resistance than coatings prepared without them. When the stabilizing polymer is nitrocellulose,

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it is preferable to include a plasticizing agent.

When tested by subjective methods the coatings of the invention, when wet, are more slippery than wet, greased glass, and, when dry, are no more slippery than dry glass. The coatings of the invention are resistant to removal by wet abrasion as determined by running water over the coatings and rubbing between tightly gripped fingers while wet. The inventive coatings have high adherence when dry, as determined by attaching adhesive tape, pulling the tape off with a vigorous action, and then wetting the coated substrate to determine whether the taped portion retained the lubricant coating. The inventive coatings remain adherent and coherent for extended periods when stored in water, and neither peel off, dissolve, nor dissociate.

The coating systems described herein will produce hydrophilic lubricant coatings, resistant to wet abrasion on surfaces such as polyethylene, polypropylene, silicon, glass, stainless steel, and other substrates generally considered as presenting adherence problems. It may be necessary to treat such surfaces with gas plasma or other ionizing treatment to promote adhesion to the substrates. The following examples show how the invention can be used.

EXAMPLE 1:

Polyurethane tubing was dip coated in a stabilizing polymer solution of

- 5.4 gm low viscosity 1/2 second nitrocellulose
- 2.0 gm dibutylphthalate
- 1.5 gm camphor

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- 1.9 gm polyvinylbutyral  
in a solvent mixture of  
36.0 ml toluene  
13.1 ml butylacetate  
5 5.9 ml isopropanol  
25.4 ml ethylacetate  
18.1 ml ethanol  
1.5 ml acetone.

The coated tube was dried for 5 minutes at 65°C. It was  
10 then dip coated with a hydrophilic polymer solution  
containing

- 6.6 gm polyvinylpyrrolidone  
63.8 ml denatured ethanol  
23.6 ml ethyl acetate  
15 12.6 ml dimethylformamide

and dried 5 minutes at 65°C. A hydrophilic coating  
resulted which was slippery when wet.

EXAMPLE 2:

- 20 Styrenebutadiene tubing was dip coated in a  
stabilizing polymer solution containing 1.9 gm 1/2  
second nitrocellulose together with a hydrophilic  
polymer, 1.5 gm polyvinylpyrrolidone, in

- 60 ml ethylacetate  
25 34.4 ml denatured ethanol  
4.6 ml acetic acid  
1 ml isopropanol

- and dried 5 minutes at 80°C. The sample was then dip  
coated in a hydrophilic polymer solution containing 7.5  
30 gm polyvinylpyrrolidone together with a stabilizing  
polymer, 0.3 gm nitrocellulose, in  
73 ml denatured ethanol

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26.8 ml ethylacetate

0.2 ml isopropanol

and dried 5 minutes at 80°C. A hydrophilic coating resulted that was lubricious when wet.

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EXAMPLE 3:

Polyurethane tubing was dip coated with a stabilizing and hydrophilic polymer solution containing 5.9 gm 1/2 sec. cellulose acetate butyrate and 5.9 gm polyvinylpyrrolidone in 33 ml ethyl acetate and 67 ml chloroform and dried 5 minutes at 80°C. This was then dip coated in a hydrophilic polymer solution containing 5 gm polyvinylpyrrolidone in 95 ml denatured ethanol and dried 5 minutes at 80°C. A hydrophilic coating resulted that was lubricious when wet.

15

EXAMPLE 4:

Samples of polyurethane tubing were coated with a stabilizing and adherent polymer solution containing

20 1.9 gm nitrocellulose  
1.1 gm polyester resin  
1.0 gm monobutylester of  
polymethylvinylether/maleic anhydride copolymer  
0.8 ml isopropanol  
25 57.8 ml ethylacetate  
33.4 ml denatured ethanol  
8 ml dimethylformamide.

The sample was dried five minutes at 80°C. The samples were then dip coated in a hydrophilic polymer solution containing

30

6.6 gm polyvinylpyrrolidone



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63.8 ml denatured ethanol

23.6 ml ethylacetate

12.6 ml dimethylformamide

The sample was dried five minutes at 80°C, to produce an  
 5 adherent, lubricious, layered coating. A similar  
 coating was also produced on polyvinylchloride tubing.

EXAMPLE 5:

This example shows how different "adhesive" resins  
 10 can be added to promote adhesion to a substrate.

a. The following stabilizing polymer solution was  
 dip coated on polyurethane tubing and dried 5 minutes at  
 80°C.

15	nitrocellulose	56 gm
	camphor	15 gm
	dibutylphthalate	20 gm
	isopropanol	23 ml
	toluene	225 ml
	ethyl acetate	330 ml
20	butyl acetate	96 ml
	acetone	7 ml

This was then dip coated with a hydrophilic polymer  
 solution:

25	polyvinylpyrrolidone (PVP)	3 gm
	denatured ethanol	27 ml
	ethyl acetate	10 ml
	dimethylformamide	12 ml

The coating separated from the tubing when immersed in  
 water.

30 b. Example 5(a) was repeated with from 5.0 gm to  
 17 gm of polyurethane resin added to the nitrocellulose  
 solution to produce samples that showed excellent

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adhesion when immersed in water.

c. Example 5(a) was repeated with from 5.0 gm to 17.0 gm polyester resin added to the nitrocellulose solution to produce samples that showed excellent  
5 adhesion when immersed in water.

d. Example 5(a) was repeated with from 5.0 gm to 17.0 gm of styrene butadiene resin added to the nitrocellulose solution to produce samples that showed excellent adhesion when immersed in water.

10 e. Example 5(a) was repeated with from 5.0 gm to 17.0 gm of urea formaldehyde resin added to the nitrocellulose solution to produce samples that showed excellent adhesion when immersed in water.

15

EXAMPLE 6

Polyurethane tubing was coated with the following stabilizing polymer solution and dried five (5) minutes at 65°C.

	nitrocellulose	65 gm
20	dibutylphthalate	24 gm
	camphor	18 gm
	polyvinylbutyral	23 gm
	acetone	28 ml
	ethanol	306 ml
25	butyl acetate	257 ml
	ethyl acetate	500 ml
	toluene	550 ml
	isopropanol	28 ml
	dimethylformamide	200 ml

30 The sample was then overcoated with the following hydrophilic polymer solution and dried five (5) minutes at 65°C.

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polyvinylpyrrolidone	1 gm
ethanol	9 ml
dimethylformamide	3 ml
water	0.5 ml

5 This sample had excellent adhesion when immersed in water.

EXAMPLE 7

10 An acrylic surface was coated with the following stabilizing polymer solution and dried five (5) minutes at 70°C.

cellulose acetate propionate	12.9 gm
dibutylphthalate	4.8 gm
camphor	3.6 gm
15 acetone	3.2 gm
ethyl acetate	55.7 gm
toluene	58.6 gm
butyl acetate	28.5 gm
isopropanol	5.6 gm

20 The sample was then coated with the following hydrophilic polymer solution and dried five (5) minutes at 70°C.

acetonitrile	5 ml
ethanol	4.5 ml
25 PVP (360,000 mw)	0.5 gm

The coating was not soluble in water and was very slippery.

EXAMPLE 8

30 An acrylic surface was coated with the following stabilizing polymer solution and dried five (5) minutes at 70°C.

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	cellulose acetate	12.9 gm
	dibutylphthalate	4.8 gm
	camphor	3.6 gm
	methylethylketone	148.3 ml
5	dimethylformamide	20.0 ml

The sample was then coated with the following hydrophilic polymer solution and dried five minutes at 70°C.

	PVP (360,000 mw)	0.5 gm
10	cellulose acetate	0.1 gm
	acetone	6 ml
	ethanol	4.5 ml
	acetic acid	1.0 ml
	methylethylketone	0.9 gm

15 The coating was insoluble in water and was very lubricious.

#### EXAMPLE 9

An acrylic surface was coated with the following stabilizing and adherent polymer solution and dried five minutes at 70°C.

	cellulose acetate butyrate	6.5 gm
	polyester resin	6.0 gm
	dibutylphthalate	2.4 gm
25	camphor	1.8 gm
	acetone	2.5 ml
	ethyl acetate	43.6 ml
	toluene	43.6 ml
	butylacetate	22.4 ml

30 The sample was then coated with the following hydrophilic polymer solution and dried five (5) minutes at 70°C.

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acetonitrile	5 ml
ethanol	4.5 ml
PVP (360,000 mw)	0.5 gm

5 This coating was water insoluble and was lubricious when wet.

EXAMPLE 10

10 Nylon tubing was coated with stabilizing polymer with the following solution and dried ten (10) minutes at 75°C.

nylon resin	2 gm
trifluoroethanol	18 ml

15 The sample was then overcoated with hydrophilic polymer with the following solution and dried ten (10) minutes at 75°C.

PVP (360,000 mw)	1.0 gm
nylon resin	0.3 gm
ethanol	9.0 ml
dimethylformamide	3.0 ml
20 trifluoroethanol	2.7 ml

This coating was not water soluble.

EXAMPLE 11

25 A stainless steel wire guide was coated with stabilizing polymer with the following solution and dried ten minutes at 70°C.

nitrocellulose	64.6 gm
dibutylphthalate	24.3 gm
camphor	17.9 gm
30 polyvinylbutyral	22.5 gm
acetone	28.4 ml
ethanol	306.1 ml

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	butylacetate	257.0 ml
	ethylacetate	499.2 ml
	toluene	552.8 ml
	isopropanol	27.5 ml
5	dimethylformamide	200.0 ml

The sample was then overcoated with hydrophilic polymer with the following solution and dried ten (10) minutes at 70°C.

	PVP	1.0 gm
10	ethanol	9.0 ml
	dimethylformamide	2.0 ml

This coating was insoluble in water and was very lubricious.

15

EXAMPLE 12

The coating method of example 11 was repeated on an acrylic surface and also produced a coating that was insoluble in water and very lubricious.

20

EXAMPLE 13

Nylon tubing was coated with a stabilizing and adherent polymer with the following solution and dried for five (5) minutes at 65°C.

	nitrocellulose	32.3 gm
25	polyurethane	11.2 gm
	dibutylphthalate	12.2 gm
	camphor	9.0 gm
	polyvinylbutyral	11.2 gm
	acetone	25 ml
30	ethanol	254 ml
	butylacetate	225.3 ml
	ethylacetate	439.2 ml

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toluene	467.8 ml
isopropanol	13.8 ml
dimethylformamide	100 ml

5 The sample was then coated with hydrophilic polymer with the following solution and dried five (5) minutes at 65°C.

PVP	1.0 gm
nitrocellulose	0.12 gm
ethanol	9.0 ml
10 dimethylformamide	3.0 ml
ethylacetate	0.4 ml

This coating was insoluble in water and was very lubricious.

15

EXAMPLE 14

Polyurethane tubing was coated with the following stabilizing polymer solution and dried five (5) minutes at 65°C.

nitrocellulose	64.6 gm
20 dibutylphthalate	24.3 gm
camphor	17.9 gm
polyvinylbutyral	22.5 gm
acetone	28.4 ml
ethanol	306.1 ml
25 butylacetate	257.0 ml
ethylacetate	449.2 ml
toluene	552.8 ml
isopropanol	27.5 ml
dimethylformamide	200.0 ml

30 This sample was then overcoated with the following hydrophilic polymer solution and dried five minutes at 65°C.

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PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	2.0 ml

This sample coating was insoluble in water and very  
5 lubricious when wet.

EXAMPLE 15

Polyvinylchloride tubing was treated in the same  
way as the nylon tubing in example 13. The resulting  
10 coating was insoluble and very lubricious.

EXAMPLE 16

A sample of styrene-butadiene tubing was coated  
with stabilizing and adherent polymer with the following  
15 solution and dried five (5) minutes at 80°C.

	nitrocellulose	32.3 gm
	polyurethane	10.0 gm
	dibutylphthalate	12.2 gm
	camphor	9.0 gm
20	polyvinylbutyral	11.2 gm
	acetone	25 ml
	ethanol	264 ml
	butylacetate	226.3 ml
	ethyl acetate	439.2 ml
25	toluene	467.8 ml
	isopropanol	13.8 ml
	dimethylformamide	100 ml

The sample was then coated with the following  
hydrophilic polymer solution and dried five minutes at  
30 80°C.

PVP	1.0 gm
ethanol	9.0 ml



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dimethylformamide	3.0 ml
water	0.5 ml

This sample was insoluble in water and was lubricious when wet.

5

EXAMPLE 17

This example shows how solvent(s) can be added which improves adhesion by etching or interacting with the layer onto which it is being coated. Several

10 samples of polyurethane tubing were coated with the following stabilizing polymer solution.

	nitrocellulose	64.6 gm
	dibutylphthalate	24.3 gm
	camphor	17.9 gm
15	polyvinylbutyral	22.5 gm
	acetone	28.4 ml
	ethanol	306.1 ml
	butylacetate	257.0 ml
	ethyl acetate	499.2 ml
20	toluene	552.8 ml
	isopropanol	27.5 ml
	dimethylformamide	200.0 ml

Samples coated as above were then coated with one of the following solutions containing various amounts of

25 dimethylformamide or acetic acid, which interact with the surface being coated in order to promote adhesion:

(a) Coat with the following hydrophilic polymer solution and dry five (5) minutes at 70°C.

	PVP	1.0 gm
30	ethanol	9.0 ml
	dimethylformamide	3.0 ml

This hydrophilic coating adhered well, was insoluble in

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water, and was very lubricious.

(b) Coat with hydrophilic polymer, 10% (w/v) PVP in ethanol and dry five (5) minutes at 70°C. This hydrophilic coating dissolved in water and came off.

5 (c) Coat with the following hydrophilic polymer solution and dry five (5) minutes at 70°C.

PVP	1.0 gm
ethanol	9.0 ml
dimethylformamide	1.0 ml

10 This sample resisted removal when wet, but was not as resistant to wet abrasion as the sample above containing three (3) ml of dimethylformamide.

(d) Coat with the following hydrophilic polymer solution and dry five (5) minutes at 70°C.

15 PVP	1.0 gm
ethanol	9.0 ml
acetic acid	3.0 ml

This hydrophilic coating adhered well, was insoluble in water, and was very lubricious.

20

#### EXAMPLE 18

In this example, the hydrophilic polymer and the stabilizing polymer were combined into a single solution, which was coated on polyurethane tubing and

25 dried five (5) minutes at 80°C:

PVP	0.5 gm
nitrocellulose	0.056 gm
methylethylketone	13.7 ml
isopropanol	0.024 gm
30 acetic acid	1.0 ml

This produced a single-layer coating that was lubricious when wet and was resistant to wet abrasion.

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EXAMPLE 19

The following solution is coated on polyurethane tubing and dried (5) minutes at 80°C.

	PVP	1.5 gm
5	Polyethylene Glycol	2.7 gm
	Ethanol	68.8 gm
	Isopropanol	18.0 gm
	4-Butyrolactone	8.0 gm

In this example, the hydrophilic polymer was combined in a solution which contains at least one solvent which swells the substrate onto which the coating is applied. By swelling the substrate, some of the hydrophilic polymer molecules become entrained in the surface of the substrate after the solvents are evaporated.

Because some of the hydrophilic polymer is tightly bound into the substrate surface, it is made resistant to wet abrasion and produces a single-layer coating that is lubricious when wet.

EXAMPLES 20-24

The following solutions are prepared, dip-coated onto an 8 french polyurethane tube, and thereafter dried for 10 minutes at 80°C.

25	<u>INGREDIENT</u>	<u>Ex. 20</u>	<u>Ex. 21</u>	<u>Ex. 22</u>	<u>Ex. 23</u>	<u>Ex. 24</u>
	10% PV Pin	4.0 g	4.0 g	4.0 g	4.0 g	4.0 g
	Benzyl Alcohol	---	24.4 g	16.0 g	16.0 g	16.0 g
	N,N, Dimethyl	---	---	7.5 g	---	---
30	Acetamide	---	---	---	---	---
	Glacial Acetic	---	---	---	7.5 g	---
	Acid					

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INGREDIENT	Ex. 20	Ex. 21	Ex. 22	Ex. 23	Ex. 24
N-Methyl-2-Pyrrolidone	---	---	---	---	7.5 g
5 Denatured Ethanol	25.3 g	---	1.8 g	1.8 g	1.8 g

To evaluate the performance of coated lubricious layers with regard to wet lubricity and wet abrasion resistance the following test method was used. After the coating was dried to remove the organic solvents, a solution of Gentian Violet (such as Cat. No. 3240 from Ricca Chemical Company) is applied to the coated surface using a brush or cotton swab. This dye is strongly absorbed into the lubricious layer, but not into the plastic substrate. Next, the dyed sample is held under cold gently running water. After rinsing the samples with water, they are rubbed briskly between the thumb and forefinger of one hand using a firm grip. In cases where adhesion to the plastic substrate is very poor, the coated layer may wash off completely from the surface as evidenced by washing off of substantially all of the dye. In cases where the coated layer has penetrated too far into and/or become too hardened as by incorporation of too much polymeric or cross-linking agent into the coating, the dye stain can be very strong after rinsing. During the finger rubbing test, most or all of such coated layers will stay on the plastic substrate, as evidenced by retention of most of the dye, but they will not feel very lubricious. Intermediate between these extremes are coatings that have a more desirable balance of lubricious feel and resistance to

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removal by wet rubbing. An ability to make such qualitative assessments is quickly developed by persons skilled in evaluating physical properties of various plastic or other materials.

5           The coating of Example 20 washed off completely when held under cold running water, indicating that there was little or no penetration into the polyurethane and hardening of the coating. This is expected since ethanol shows very low solvent activity  
10 toward this polyurethane surface.

          The outermost portion of the coatings of Examples 21 and 23 rubbed off when wet, but a thin layer remained that was very lubricious. The retained dye intensity was intermediate. These samples were judged  
15 to have very good balance between resistance to wet abrasion and lubricity.

          The coatings of Examples 22 and 24 were not very lubricious when wet rubbed and the coating did not feel swollen by water in comparison to Examples 21 and  
20 23. Samples were extremely resistant to rubbing off when wet as evidenced by a much more intense residual dye stain after wet rubbing when compared to Examples 21 and 23. These are examples where the solvent is too active so that little lubricity results.

25           These samples show how the performance of the lubricious layer can be adjusted to balance the resistance to wet rub off and the lubricity by selecting and using solvents alone or in combination that provide a sufficient degree of activity.

30

#### EXAMPLE 25

A solution was made as follows:

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Polyvinylpyrrolidone	0.4 g
Denatured Ethanol	19.6 g
Benzyl Alcohol	10.0 g

This solution was dip coated on polyurethane tubing and then drying for 22 minutes at 80°C. A solution of Gentian Violet is applied to the coated surface as detailed in Examples 20-24. When tested, this coating was fairly resistant to wet ruff-off and was very lubricious. Comparing it to the coating of Example 21, it was a little more lubricious, but it was somewhat less resistant to wet rub-off.

#### EXAMPLE 26

The following solution was dip coated over polyurethane tubing and dried 12 minutes at 80°C. A solution of Gentian Violet is applied to the coated surface as detailed in Examples 20-24.

	Polyvinylpyrrolidone	0.4 g
	Benzyl Alcohol	10.5 g
20	Denatured Ethanol	3.6 g
	N,N, Dimethylacetamide	5.0 g

This coating was very lubricious and a lubricious layer remained on the surface after vigorous wet rubbing which would not be removed.

25

#### EXAMPLE 27

The following solution was dip coated on polyvinyl chloride tubing and dried 12 minutes at 80°C.

30	Polyvinyl Pyrrolidone	0.9 gm
	Methyline Chloride	5.0 gm
	N-Methyl-2-Pyrrolidone	10.0 gm

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A solution of Gentian Violet is applied to the coated surface as detailed in Examples 20-24. After cooling, the coating was tested for wet lubricity and wet rub resistance by using the aforementioned Gentian Violet test regimen.

This coating was very lubricious and a lubricious layer remained on the surface after vigorous wet rubbing which could not be removed.

The examples provided above are not meant to be exclusive. Many other variations of the present invention, including the use of other cosolvents and polymer mixtures, would be obvious to those skilled in the art, and are contemplated to be within the scope of the appended claims.

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CLAIMS

1. A lubricious hydrophilic coating for an article which is substantially more slippery when wet than when dry, resistant to removal by wet abrasion and essentially insoluble in aqueous solution comprising a hydrophilic polymer selected from the group consisting of polyvinylpyrrolidone and polyvinylpyrrolidone-polyvinyl acetate copolymer, and a mixture of the above, and a water-insoluble stabilizing polymer consisting essentially of a cellulose ester, a copolymer of polymethyl vinyl ether and maleic anhydride, an ester of the copolymer, nylon, and a mixture of any of the foregoing.

2. The coating of claim 1 which is applied to the surface of a polymer selected from the group consisting of glass, metal, polyurethane, polyvinylchloride, polyacrylate, polycarbonate, polystyrene, polyester resins, polybutadiene-styrene copolymers, nylon, polypropylene, and polybutylene.

3. An article having the lubricious hydrophilic coating of claim 1.

4. The coating of claim 1 in which the stabilizing polymer is concentrated in the inside portion of the coating adjacent the surface of the article and the hydrophilic polymer is concentrated in the outer portion of the coating.

5. An article having a lubricious hydrophilic coating, comprising  
an article having a polymer surface, and  
a lubricious hydrophilic coating on said



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substrate, said hydrophilic coating including a hydrophilic polymer selected from the group consisting of polyvinylpyrrolidone, polyvinylpyrrolidone polyvinyl acetate copolymer, and a mixture of the above, said hydrophilic coating having an exposed outer surface and an interfacing surface with said polymer surface, said hydrophilic coating having a high degree of cross-linking or intermolecular mingling between said hydrophilic polymer and said polymer surface at said interfacing surface relative to said outer surface,

said hydrophilic coating being substantially more slippery when wet than when dry, resistant to removal by wet abrasion, and essentially insoluble in aqueous solution.

6. The article of claim 5, wherein said polymer surface comprises polyvinylchloride, polyacrylate, polycarbonate, polystyrene, polyester resins, polybutadiene-styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon, and polyvinyl acetal.

7. An article having a lubricious hydrophilic coating, comprising

an article having a polymer surface selected from the group consisting of polyurethane, polyvinylchloride, polyacrylate, polycarbonate, polystyrene, polyester resins, polybutadiene-styrene copolymers, nylon, polypropylene, polybutylene, teflon, silicon, and polyvinyl acetal, and

a lubricious hydrophilic coating on said substrate, surface with said polymer surface, said hydrophilic coating having an exposed outer surface and an interfacing said hydrophilic coating including a

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hydrophilic polymer selected from the group consisting of polyvinylpyrrolidone, polyvinylpyrrolidone polyvinyl acetate copolymers, and a mixture of the above,

said hydrophilic coating penetrating said polymer surface of said polymer surface via the use of a cosolvent for both said hydrophilic polymer and said polymer surface during application of said hydrophilic coating, said hydrophilic coating having a high degree of cross-linking or intermolecular mingling between said hydrophilic polymer and said polymer surface at said interfacing surface relative to said outer surface,

said coating being substantially more slippery when wet than when dry and resistant to removal by wet abrasion.

8. An article having a lubricious hydrophilic coating, comprising

an article having a polymer surface comprising polyurethane, and

a lubricious hydrophilic coating comprising polyvinylpyrrolidone, said hydrophilic coating penetrating said polymer surface of said substrate via use of a cosolvent for both polyvinylpyrrolidone and polyurethane, said hydrophilic coating having an exposed outer surface and an interfacing surface with said polymer surface, said hydrophilic coating having a high degree of cross-linking or intermolecular mingling between the polyvinylpyrrolidone and polyurethane at said interfacing surface relative to said outer surface,

said hydrophilic coating being substantially more slippery when wet than when dry, resistant to removal by wet abrasion, and essentially insoluble in aqueous solution, the degree of lubricity and resistance

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to wet removal being controlled in part by the particular cosolvent or cosolvent mixture used and the amount of cosolvent used.

9. A lubricious composite, comprising an outer layer having an exposed outer surface, said outer layer comprising a hydrophilic polymer selected from the group consisting of polyvinylpyrrolidone and polyvinylpyrrolidone-polyvinyl acetate copolymer, and a mixture of the above,

an inner layer comprising a water-insoluble stabilizing polymer selected from the group consisting of a cellulose ester, a copolymer of polymethyl vinyl ether and maleic anhydride, an ester of the copolymer, nylon, and a mixture of any of the foregoing,

said composite being substantially more slippery when wet than when dry, resistant to removal by wet abrasion, and essentially insoluble in aqueous solution, the ratio of said hydrophilic polymer to said stabilizing polymer altering the degree of wet lubricity, resistance to removal and insolubility of said composite.

10. An article having the lubricious composite coating of claim 9.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/US91/00771

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC (5): B32B 27/36

U.S. CL: 428/412, 421, 423.3, 423.7; 424.4, 424.6, 463, 516

## II. FIELDS SEARCHED

Minimum Documentation Searched ?

Classification System

Classification Symbols

U.S. 428/412, 425.6, 423.3, 423.5, 423.7, 424.6, 430, 435, 441, 458, 480, 474.9, 476.9, 516, 517; 525/303

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched \*

## III. DOCUMENTS CONSIDERED TO BE RELEVANT \*

Category *	Citation of Document, " with indication, where appropriate, of the relevant passages "2	Relevant to Claim No. "3
A	US, A, 3,914,341 (KLIMENT ET AL) 21 OCTOBER 1975; (see entire document).	1-10
A	US, A, 3,939,049 (RATNER ET AL) 17 FEBRUARY 1976; (see entire document).	1-10
A	US, A, 3,975,350 (HUDGIN ET AL) 17 AUGUST 1976; (see entire document).	1-10

\* Special categories of cited documents: 10

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"Δ" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

24 MARCH 1991

Date of Mailing of this International Search Report

22 APR 1991

International Searching Authority

ISA/US

Signature of Authorized Officer

E. Rollins Buffalo